

Simultaneous Cu doping and growth of TiO₂ nanocrystalline array film as a glucose biosensor

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Abstract: We present a novel strategy for simultaneous doping of Cu ions into TiO₂ nanocrystals and transforming amorphous anodic TiO₂ nanotubes (TNTs) into anatase nanoparticle (NP) array film. Highly reactive colloidal Cu clusters derived by laser ablation in liquids were used as doping precursor, which can react with amorphous TiO₂ nanotubes to form doped anatase NPs by dissolution and recrystallization processes. The Cu-doped TiO₂ NPs (Cu-TNPs) film was characterized by X-ray diffraction, scanning and transmission electron microscopy and Raman spectroscopy. The Cu-TNPs show a rugby-like shape with exposed active {101}, {001} facets and the long-axis parallel to [001] lattice direction. The substitutional Cu²⁺ ions dopants in TiO₂ nanocrystals caused the swelling of the crystalline unit cell, red shift of the absorption edge, and enhanced absorption in the visible-light region. The green and efficient doping design would facilitate the ongoing effort toward improving nanostructured TiO₂ as a practical biosensor for glucose molecules.

Keywords: Cu-doping, TiO₂, Nanocrystalline, array, Biosensor

Introduction

Titanium dioxide (TiO₂) is a potential biomaterial of great interest in biomedical fields, e.g., bone reconstruction, intravascular stents, drug delivery, biosensing for high stability, nontoxicity, low cost and so on.¹ Since Cosnier and coworkers reported that mesoporous TiO₂ films could work as glucose biosensor by immobilizing enzyme molecules under an amperometric approach in 1997,² the application of various nanostructured TiO₂ to combine with glucose oxidase was the main aspect in the fabrication of a sensitive and stable biosensor. Although the sensitivity and stability are further improved through designing new nanostructures and/or loading new chemical substances,¹ the difficulties from immobilizing enzyme, storing at lower temperature, prolonging validity and lowering cost of the device are still troublesome. So, it has become an important endeavor to substitute economical and durable inorganic electrochemical catalysts (metals, alloys and metal oxides) for fragile enzymes because these active materials could directly catalyze the electrochemical oxidation of glucose molecules in alkaline media. For example, Yu et al. had proved that TiO₂ nanotubes decorated with Ni nanoparticles displayed high catalytic electroactivity for the oxidation of glucose with the detection limit of 2 μM,³ and Li and coworkers had enhanced the sensitivity to 1590.9 μM mM⁻¹ cm⁻² by loading Ni-Cu alloy nanoparticles on TiO₂ nanotubes.⁴ Meanwhile, Luo et al. had reported that CuO nanofibers modified TiO₂ nanotubes in glucose sensing was of a low sensitivity of 79.79 μM mM⁻¹ cm⁻², but a good detection limit of 1 μM.⁵

Even though above catalysts displayed satisfied performances by combining with nanostructured TiO₂ whose large specific surface areas could facilitate to improve sensitivity and stability of the device, new challenges are still ensuing. On the one hand, note that the real active catalytic centers are the oxidized species of catalytic metal, which are usually oxidized before sensing and function as active electron-transfer mediators after absorbing glucose molecules.⁶ The metal decorated on TiO₂ usually suffers multiple cyclic voltammetry (CV) sweeping in strong alkali solution to incite increasing number of oxidized species as active sites for metal catalysis. However, this pre-treatment step compels TiO₂ to venture on the erosion in strong alkali solution. Herein, directly combining the metal oxide with TiO₂ is desirable for fast and simple sensing detection in application. On the other hand, the electrode needs an extra polymer binder (such as Nafion) to immobilize TiO₂ sensor. It may reduce catalytic active sites and then degrade the glucose sensitivity, and the inevitable separation of the TiO₂ sensor from the electrode after persistent operation can lead to loss in electrochemical activity.⁴ Moreover, synthesizing of specimens via common chemical approaches could introduce contaminations from other chemicals, which would impair the biocompatibility of TiO₂ in sensing process.⁷ Under overall analysis, an approach to combine oxidized species of catalytic metal with TiO₂ fixed or in-situ grown on the conductive substrate through a green and convenient method is thus desirable right now.

Doping is an effective way to introduce ions or oxidized species of metal into compounds. There are various methods such as sol-gel,⁸ magnetron sputtering,⁹ and solution impregnation,¹⁰ have been proposed for doping metal ions in TiO₂ for photocatalysis and biosensor. However, achieving green and uniform doping in TiO₂ crystalline lattice and simultaneously immobilizing the as-formed doped composite on a fixed substrate remains a challenge. Particularly for doping in nanoscale crystals, the self-purification effect of nanoscale crystalline even results in segregation or accumulation of impurities on surfaces or grain boundaries.^{11,12} Many reports have proved that TiO₂ nanotubes (TNTs) array film could be in-situ anodized on Ti substrate to form a Schottky-type contact which enhanced the rapid transport of surface reaction electrons to Ti substrate in biosensing,⁴ but reserving the array structure after doping is difficult. An appropriate and green doping strategy to get uniform

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distribution of impurities in TiO_2 array structure together with immobilized Ti substrate is favor for practical film applications.

Laser ablation in liquid (LAL) is a facile and green technique to obtain high purity nanocrystals with unique physicochemical properties.¹³⁻¹⁶ LAL employs the high temperatures and high pressure characteristics in laser-induced plasma plume, which lead to unsaturated valences and defects on the surface of the resulted nanocrystals because of the nonequilibrium growth processes.¹⁵ Here, to use the array structure of TNTs as an immobilized substrate, we intentionally select LAL-derived reactive Cu colloid as the precursor of dopants. We demonstrated the efficiency of in-situ doping of Cu^{2+} ions in TiO_2 in a dissolution–recrystallization process under hydrothermal treatment. The doped TiO_2 nanoparticles (NPs)-assembled array structure was characterized with the use of field-emission scanning electron microscopy (FESEM), a high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), and Raman spectrometry. The Cu^{2+} ions dopants in anatase nanocrystals increased the swelling of crystal unit cell, as well as the redshift of absorption edge, and the absorption in the visible-light region.

Experimental

Preparation of TNTs by anodic oxidation of Ti

A 0.25 mm thick Ti foil (99.99%) was sequentially cleaned in acetone, ethyl alcohol, and water under sonication, and then dried in air at room temperature. All of the chemical solvents and reagents are analytical grade. The anodizing electrolyte is ethylene glycol solvent containing 0.25 wt% NH_4F and 2 vol% H_2O . One side of the metal Ti foil contact with the electrolyte through a 15 cm diameter O-ring. Graphite was used as the counter electrode in a two-electrode cell. Anodic oxidation was conducted at room temperature for 90 min at a DC voltage of 60 V. After repeated washing with deionized water and drying, some pieces of the as-formed TNTs films were annealed at 450 °C for 2 h for the subsequent comparative experiments and some films were kept amorphous for hydrothermal procedure.

Hydrothermal treatment of LAL-derived Cu colloid and TNTs film

Colloidal Cu solution was prepared by LAL technique. Briefly, a Cu target (99.99%) was immobilized on a supporter in a vessel filled with 15 mL deionized water. The Cu target was then irradiated for 10 min by an Nd/YAG pulsed laser with 1064 nm wavelength, 10 Hz frequency, 10 ns pulse duration, and 100 mJ/pulse energy. The fresh colloid was sealed in an autoclave containing a piece of amorphous TNTs film. The hydrothermal reaction proceeded for 15 h at 200 °C. After the reaction, the film was obtained and repeatedly washed in deionized water, and finally dried for further investigations.

Structural characterization and properties of Cu-doped TiO_2 NP film

An FEI Sirion 200 FESEM was used to evaluate the morphology of the film product. The crystalline structure was investigated on HRTEM (JEM, JEOL-2010). In TEM sample preparation, small amount of the product was stripped from the Ti metal substrate and then ultrasonically dispersed in ethanol, and the obtained suspensions were then dropped onto a holey-carbon coated tungsten-grid. The phase structure was investigated by using XRD with the use of a Philips diffractometer (X'pert Pro) with Cu-K α radiation ($\lambda = 1.5419 \text{ \AA}$). Electrochemical CV spectra, amperometric curves, and impedance spectra curves of the Cu-doped TiO_2 NPs (Cu-TNPs) and blank anatase TNTs were obtained through a Zahner IM6e Electrochemical Workstation to investigate the response as nonenzymatic glucose biosensors. Zeta potential of the Cu colloid was measured by a Zetasizer 3000 HSa.

The structural features of Cu-TNPs and annealed anatase TNTs without hydrothermal treatment were further analyzed through X-ray absorption fine structure (XAFS) spectrometer, including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). The XAFS spectra for Cu-K edge of the Cu-TNPs and Ti-K edge of the two anatase TNTs samples (sample annealed at 450 °C and hydrothermally treated sample) were obtained by using beamline BL14W1, belonging to Shanghai synchrotron radiation, administrated by Shanghai Institute of Applied Physics (Shanghai, China). Transmission (standard Cu foil, Cu_2O , and CuO) and fluorescence yield (Cu-TNPs and TNTs) spectra were obtained with the use of a double-crystal Si (111) monochromator, ion chambers, and a Ge solid-state detector equipped with Ni filter. The XAFS data were analyzed through an Athena program. Cu foil, Cu_2O , and CuO were used to extract the experimental XANES features of the Cu metal, Cu^+ , and Cu^{2+} ions, respectively.

Results and discussion

Figs. 1a and 1b show the top and side view images (inserted plot) of the anodized TNTs before and after hydrothermal-treatment. The original TNTs-like shape disappeared and only the NPs accumulated which was depicted as a Cu-TNPs film array on the Ti substrate. Fig. 1b shows the compact assembly array of irregular NPs, with an average particle size of <100 nm standing on the upper surface of Cu-TNPs film. Seeing from the inserted plot in Fig. 1b, the NPs accumulated one by one along the direction of the original TNTs.

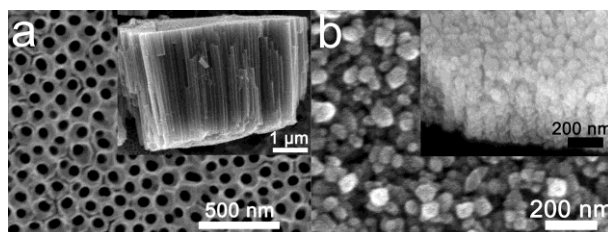


Fig. 1 Top and side views (inserted plot) of the amorphous TNTs (a) and Cu doped-TNPs (b).

HRTEM investigation provides more detailed structure and phase information. Fig. 2a shows a single particle in a rugby-like shape. The partial zone in the white rectangle was magnified in Fig. 2b and the corresponding selected area electron diffraction (SAED) pattern is shown in Fig. 2c. The lattice spacings of 4.74 and 3.53 Å correspond to (002) and (101) crystalline planes of the anatase TiO_2 , the angle between the two planes (68.3°) is consistent with the standard data. The crystals grew along the long-axis of ellipsoid that is parallel to [001] lattice direction with the exposed active {100} and {101} facets. Corresponding to the assembled NPs in Fig. 2d, the elemental mapping images in Figs. 2e, 2f, and 2g display the dispersion of O, Ti, and Cu, respectively, in the accumulated NPs. The amount of Cu was significantly lesser than the other two elements. The result of energy-dispersive X-ray spectroscopy shows that the atomic ratio of Ti and Cu was 16.35 to 0.4 (Fig. S1 in ESI†).

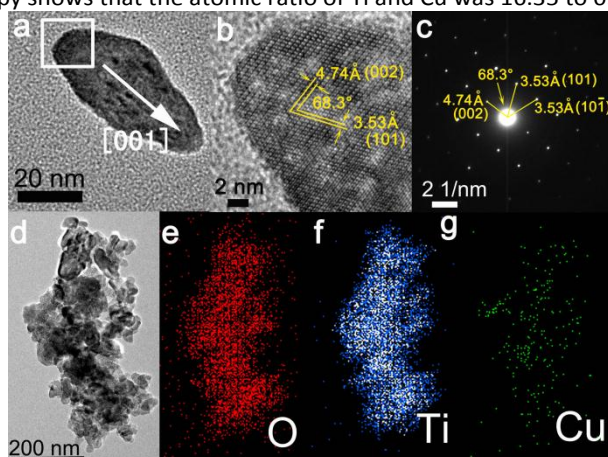


Fig. 2 (a) TEM image of a single Cu-TNPs; (b) magnified image of NP in (a); (c) corresponding SAED pattern of NP in (b); and (d) TEM image of accumulated NPs. (e-g) Elemental mapping images of O, Ti, and Cu corresponding to that in (d).

The XRD pattern shows the composition and structural information of the products. For comparison, TNTs samples were also annealed at 450°C for 2 h to form pure anatase phase. The XRD results (Fig. 3) indicated no significant difference between the anatase TNTs (red curve) and the Cu-TNPs (blue curve). All of the peaks are consistent with the data of standard cards [JCPDS card No. 21-1272 (anatase TiO_2) and JCPDS card No. 44-1294 (hexagonal Ti)]. The observed phases were consistent with the HRTEM analysis. However, three peaks at 25.4° (101), 48.0° (200), and 63.0° (204) of the anatase TNTs film a little shifted to the low-angle direction, thereby leading to the increase in d-spacings of (101), (200), and (204) planes from 3.520, 1.892, and 1.480 Å to 3.532, 1.901 and 1.487 Å, respectively. According to Equation (S1) in ESI for tetragonal-system compounds, the change in unit cell parameters (a, b, c) could be deduced. In this study, the a and c values increased from 3.785 and 9.513 Å to 3.803 and 9.543 Å in the anatase structure. The distortion of anatase lattice could be due to the doping of Cu species in the inner sites of original lattices.

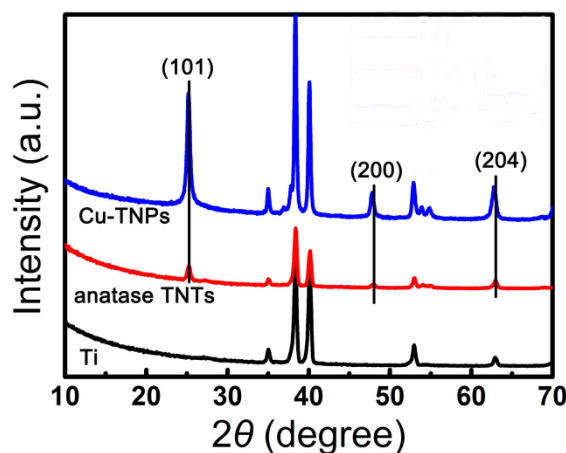


Fig. 3 XRD spectra of Cu-TNPs, anatase TNTs, and metal Ti foil.

Figure 4 shows the Raman spectra of the annealed TNTs (black curve) and Cu-TNPs (red curve). The four typical Raman peaks of the anatase phase were found at 147 cm^{-1} (E_g mode), 399 cm^{-1} (B_{1g} mode), 517 cm^{-1} (both A_{1g} and B_{1g} modes), and 637 cm^{-1} (E_g mode) for the TNTs sample.¹⁷ The dominant phase of Cu-TNPs is also the anatase TiO_2 structure as XRD results. Similar to many reports about introducing metal ions into TiO_2 lattice by substitutional strategy,^{18,19} Raman active modes of Cu-TNPs slightly shifted to lower frequency zone, respectively at 145 cm^{-1} , 397 cm^{-1} , 515 cm^{-1} and 627 cm^{-1} . Based on the extensive energetic computation results, it was especially easier for transition metals to substitute Ti sites than to form interstitial defects.²⁰ Here, we proposed that the shift of Raman peaks was due to the enlargement of anatase lattice by substitutional doping of Cu ions.

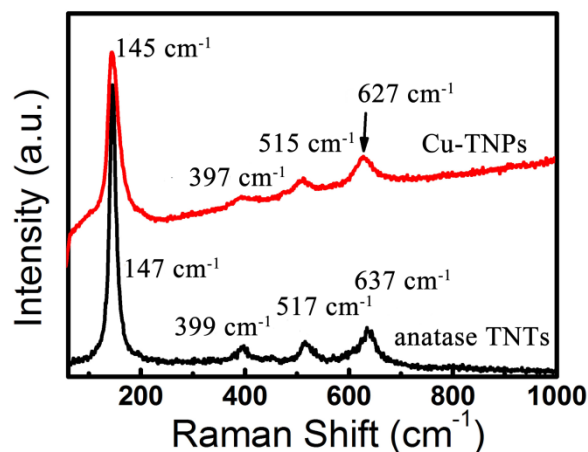


Fig. 4 Raman spectra of Cu-TNPs and anatase TNTs.

Fig. 5a shows the Cu K-edge XAFS spectra of the Cu foil, Cu_2O , CuO, and the as-prepared Cu-TNPs, and Fig. 5b shows the corresponding XANES spectra of these samples at the pre-edge region. In the XAFS spectrum, it is obvious to find that the dominant main peak and the shoulder peaks at the post-edge region of the Cu-TNPs most resembled those of CuO. In the XANES spectra, the pre-edge peaks were always intrinsic for various Cu ions species.²¹ The characteristic peaks of the Cu^{2+} ions were found at (i) approximately 8976 eV to 8979 eV (a very weak absorption caused by the dipole-forbidden $1s \rightarrow 3d$ electronic transition), and (ii) at approximately 8985 eV to 8988 eV as a shoulder peak, as well as at approximately 8995 eV to 8998 eV as an intense peak (both attributed to the $1s \rightarrow 4p$ transition). The Cu^+ ions are normally discriminated by a single peak at 8983 eV to 8984 eV. In Fig. 5b, peak A at 8978 eV and peak B at 8986 eV were observed for CuO, whereas the peaks C and D were found at 8983 and 8982 eV, respectively, which correspond to the pre-edge absorption of Cu^+ ions in Cu_2O and Cu atoms in the Cu foil. For the Cu-TNPs, the weak pre-edge absorption at 8978 eV (peak A) and the intense peak between 8995 eV and 8998 eV both belong to Cu^{2+} ions were found. However, the pre-edge shoulder peak B wasn't observed probably due to the low concentration of dopants. Therefore, the oxidation state of the Cu species in the Cu-TNPs sample was Cu^{2+} ions. The post-edge region of the XAFS spectrum (EXAFS) could be presented in energy space, such as in Fig. 5a and 5b. EXAFS could also be shown in wave-vector space (k space) with the use of k^3 -weighted Fourier transform in Athena programs. Fig. S2a in ESI shows the EXAFS spectra of the Ti K-edge absorption of the annealed TNT sample without hydrothermal treatment and the Cu-TNPs sample, while Fig. S2b compares the Cu K-edge EXAFS spectra of Cu foil, Cu_2O , CuO and Cu-TNPs in k -space. The Ti K-edge curves for the annealed TNTs (black) and the Cu-TNPs (red) were almost the same. Therefore, the coordination environments have no significant variation for the Ti^{4+} ions in the anatase TiO_2 with and without hydrothermal treatment. For the Cu-TNPs Cu K-edge in Fig. S2b, the oscillation trend in the k -space apparently departed from the other three curves of Cu foil, Cu_2O , CuO, respectively. This phenomenon further proved that the coordination circumstances of the dopants in anatase lattice varied with Cu species in metal Cu or oxides. We could thus assume that the dopants did not change the anatase lattice environment largely, which was consistent with the above data analysis.

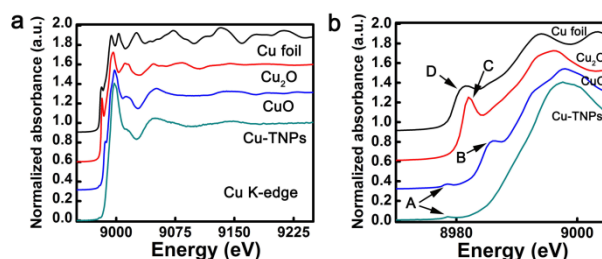


Fig. 5 (a) XAFS spectra of Cu foil, Cu_2O , CuO, and Cu-TNPs; (b) XANES spectra of Cu foil, Cu_2O , CuO, and Cu-TNPs in (a).

Figure 6 was the general schematic view of the formation of Cu TNPs array film from TNTs array film with a simultaneous doping process. Amorphous TNTs could dissolve in situ as TiO_6 octahedral unit in water under hydrothermal conditions and then recrystallize as anatase NPs, which are inclined to deposit at the undissolved surfaces of TNTs.²² These NPs accumulate along the direction of original array after absolute dissolution of the TNT film. For the anatase phase of TiO_2 , each octahedral TiO_6 unit is

connected with other four units by edge-sharing and with another four by corner-sharing. In addition, the surface of TiO_6 was negatively charged because of the surplus of O^{2-} ions, whereas the zeta potential of the as-formed colloid was approximately +23.5 mV, thereby indicating that the surfaces of LAL-generated colloidal Cu clusters were positively charged. The electrostatic attraction results in Cu doping during the recrystallization process. As substitutional dopants in the lattice, Cu^{2+} ions can occupy the site of Ti^{4+} ions in TiO_6 octahedrons.²³ Although less bonding of the substitutional species with the nearest O^{2-} ions could not be neglected totally, the major role of larger Cu^{2+} ions was to swell the unit cell in accordance with the enlarged *a* and *c* lattice parameters according to XRD, Raman and XAFS analysis.



Fig. 6 Schematic illustration of formation of Cu TNPs array film.

Cu is famous in oxidizing carbohydrate without surface poisoning in biosensing.²⁴ Glucose is a typical biosensing target because it is essential to organisms, and electrochemical technology is a popular technique for biosensing assessment. All of the tests were conducted with the use of saturated Ag/AgCl as the reference electrode and Pt foil as the counter electrode. Both the anatase TNTs and the Cu-TNPs were used as working electrodes and sealed with the use of an epoxy resin, leaving an exposed area of 7 cm^2 on the top surface. Fig. 7a shows the CV sweeps of the two samples in 0.1 M NaOH aqueous solutions with and without 10 mM glucose solute. The sweeping at 50 mV/s was from 0 V to +0.8 V and then back to 0 V. Curves A and B, which are for the anatase TNTs, are close to rectangles and did not show any response triggered by the absorbed molecules on the surface of the electrode. Curve C also did not display any oxidation or reduction peaks. Only curve D showed an apparent current response at approximately +0.65 V, which was attributed to the oxidation peak of glucose on active $\text{Cu}^{2+}/\text{Cu}^{3+}$ electron-transfer mediators.²⁵

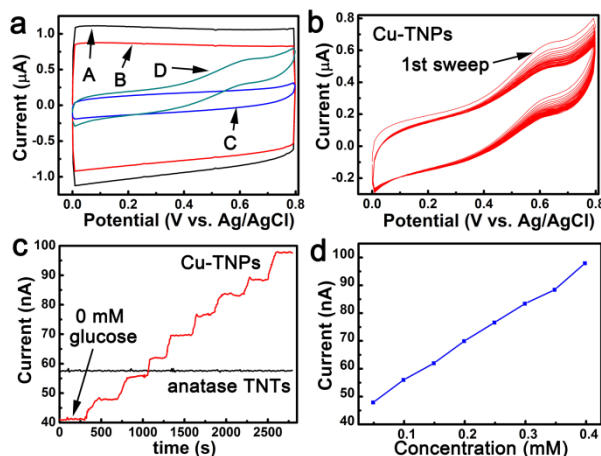
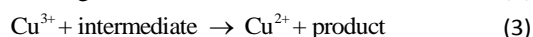
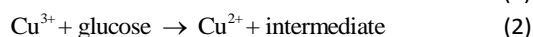


Fig. 7 (a) CV sweeping of anatase TNTs in 0.1 M NaOH solution (curve A) and in 0.1 M NaOH solution with 10 mM glucose (curve B); Cu-TNPs in 0.1 M NaOH solution (curve C) and in 0.1 M NaOH solution with 10 mM glucose (curve D). (b) 30 times CV sweeping of Cu-TNPs in 0.1 M NaOH solution with 10 mM glucose. (c) Amperometric response of Cu-TNPs and anatase TNTs at +0.65 V with successive addition of 7.5 μL glucose solution (100 mM) at 5 min intervals in 15 mL NaOH solution (0.1 M). (d) Linear relationship between the oxidation current of Cu-TNPs and glucose concentration.

The reaction processes⁶ are described with the use of Equations (1), (2), and (3). Without pre-oxidation of the electrode, the Cu^{2+} ions in the TiO_2 NPs could directly function as active sites for glucose oxidation. The 30 successive sweeps in NaOH solution with glucose (Fig. 7b) confirmed that the doped electrode was stable under CV. Fig. 7c shows the amperometric responses of the anatase TNTs and the Cu-TNPs with added 7.5 μL pure glucose aqueous solution (100 mM) at 5 min intervals in 15 mL NaOH solution (0.1 M) under +0.65 V oxidation potential. No significant current response was found for the anatase TNTs, whereas the current increased significantly at each addition of glucose for the Cu-TNPs. The initial current response of the anatase TNTs was higher than that of Cu-TNPs, which is possibly due to the enhanced interfacial impedance of the accumulation NPs (Fig. S3, see ESI). Fig. 7d shows the linear relationship between the response current of Cu-TNPs and the concentration of

glucose in NaOH solution. This relationship directly reflected the fast and stable sensor behaviours of Cu-TNPs in response to glucose molecules.



Conclusions

In summary, we developed an efficient doping and in-situ phase modification route to obtain Cu-doped TiO₂ nanocrystalline film by hydrothermal treatment with the use of anodic TNTs and LAL-derived colloidal Cu clusters as precursors. The Cu-doped anatase NPs accumulated one by one along the original direction of the initial amorphous TNTs, thereby resulting in a new TiO₂ NPs film on the immobilized Ti substrate. The unique array morphology was observed even after TNTs dissolution and in-situ phase transition from amorphous TiO₂ to rugby-shaped single-crystal TiO₂ NPs with preferred [001] long-axis growth direction and exposed active {001}, {101} facets. The substitutional Cu dopants in the anatase nanocrystals caused the swelling of crystal unit cell, obvious red shift of absorption edge, and enhanced absorption in the visible-light region. The film showed an excellent biosensing performance in the electrochemical test with the use of glucose molecules as targets. The present experimental design for fabricating doped-TiO₂ NPs film on immobilized substrate could be extended to the construction of similar structures for device in other applications.

Acknowledgements

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